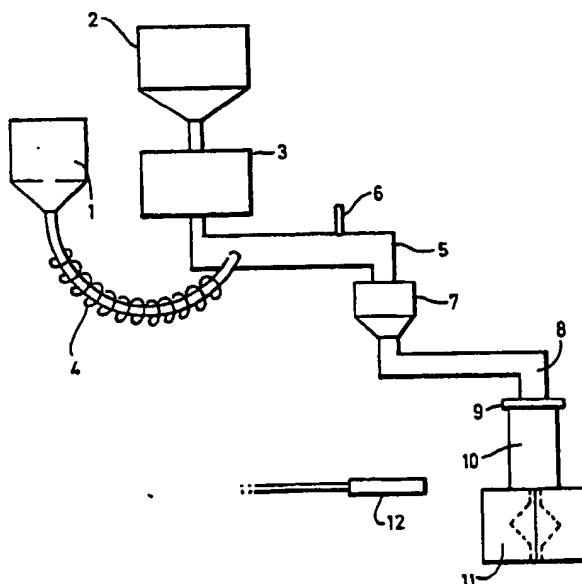




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B22C 5/08, 5/04, 9/12		A1	(11) International Publication Number: WO 93/19870
			(43) International Publication Date: 14 October 1993 (14.10.93)
(21) International Application Number: PCT/GB93/00636 (22) International Filing Date: 29 March 1993 (29.03.93) (30) Priority data: 9206835.2 28 March 1992 (28.03.92) GB 9210615.2 19 May 1992 (19.05.92) GB (71) Applicant (for all designated States except US): BORDEN (UK) LIMITED [GB/GB]; Rownhams Road, North Baddesley, Southampton SO52 9ZB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): MELLING, Richard [GB/GB]; The Old School House, Rhewl, Nr Ruthin, Clwyd LL15 2TU (GB). DODD, Stephen, Francis [GB/GB]; 2 Camrau, Cefn, Nr St. Asaph, Clwyd LL17 0HG (GB).		(74) Agent: WILKINSON, Stephen, John; Stevens, Hewlett & Perkins, 1 St Augustine's Place, Bristol BS1 4UD (GB). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.	

(54) Title: A METHOD FOR MAKING MOULDS



(57) Abstract

A method for making a mould used in the manufacture of foundry castings comprises (a) providing a water-insoluble particulate material, such as sand; (b) combining the particulate material with a binder, preferably containing polyphosphate chains and/or borate ions and water; (c) heating the mixture to a temperature in excess of 100 °C; (d) forming the mixture into a desired shape; and removing water from the mixture, with air, at a temperature in excess of 100 °C. The method ensures that the volatilisation of the water does not cool the mixture and, therefore, the production cycle is hastened and efficiency is improved.

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A Method for Making Moulds

This invention relates to water dispersible moulds which are used in the manufacture of foundry castings. More particularly it relates to a method for making such moulds.

The term "mould" as used in this specification includes both a mould for producing castings with or without cavities and a core for producing a cavity in a cavity containing casting and combinations of such moulds and cores.

Cores and moulds are made from sand or other refractory particulate materials and it is customary to add binders in order to give the necessary properties of flowability (to enable the core/mould to be formed), stripping strength (to enable the core/mould to be handled soon after forming) and the ultimate strength to withstand the conditions occurring during casting.

The refractory particulate material and binder are formed into a core or a mould by various processes which include ramming, pressing, blowing and extruding the mix into a suitable forming means such as a core box, a moulding flask, or a moulding or mould box.

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Water is present in the mix of refractory particulate material and binder, and must be removed after the core or mould has been formed in the forming means, and before it can be used in the manufacture of foundry castings. In one method, after the mix has been formed into a core in a core box, the core box is heated to a temperature in the range of 50-90°C, and then purged with compressed air at a pressure of 80 pounds per square inch for a period of time in excess of 30 seconds depending on the core size and binder composition.

This removal of water by evaporation requires relatively large amounts of heat (ie the latent heat of vaporization), and so the drying action of the air flow has a cooling effect which hinders further evaporation thereby extending cycle times.

Once enough water has been removed from the core so that it can be handled without being damaged, the core is then transferred to an oven where final removal of water is accomplished by heating the core to a temperature in the range 120-150°C.

According to an aspect of the present invention there is provided a method for making a mould used in the manufacture of foundry castings, the method comprising the steps of:

- (a) providing a water insoluble particulate material;
- (b) combining the particulate material with a binder;
- (c) heating the mixture of particulate material and binder to a temperature in excess of 100°C;

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- (d) forming the particulate material and binder mixture into a desired shape;
- (e) removing water from the mixture with air at a temperature in excess of 100°C.

In a preferred embodiment of the invention the steps (b) to (d) are carried out in a saturated atmosphere of steam.

As the steps (c) to (e) are carried out at temperatures in excess of 100°C no latent heat of vaporization is required and there is no cooling effect caused by vaporization. Consequently the purge time of the core is significantly reduced. Furthermore by using this method it has been found that the final drying step in an oven at temperatures in excess of 100°C is no longer necessary.

In the method of the invention, the binder may be any composition which after being mixed with the water-insoluble particulate material in the presence of water is capable of binding together the particles of the water-insoluble particulate material upon removal of water (e.g., by volatilisation) from the mixture. For example, the method of the invention may utilise silicate binders, for instance alkali metal silicate, and other inorganic binding materials.

Preferably the binder includes polyphosphate chains and/or borate ions, and even more preferably these are respectively derived from at least one water soluble phosphate and/or borate glass. The binder may be added to the particulate material as an aqueous solution. Alternatively, the binder and the particulate material may be mixed together and then water may be added to the mixture.

In one preferred embodiment the binder has been mixed with the particulate material in the form of an aqueous solution of the at least one water soluble glass.

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In another preferred embodiment, the binder has been mixed with the particulate material in the form of particles of the at least one water soluble glass and the polyphosphate chains and/or borate ions have been formed by mixing water with the mixture of particulate material and glass particles. The glass particles may be wholly or partially dissolved into the water thereby to form the polyphosphate chains and/or borate ions.

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The water-soluble glass may be wholly vitreous or partially devitrified, in the latter case the water-soluble glass having been heated and cooled thereby to form crystalline regions in an amorphous or glassy phase.

Without wishing to be bound by theory, it is believed that the polyphosphate chains are formed following the dissolution of the respective water soluble glasses into aqueous solution. These chains form an interlinking matrix throughout the mould, which is enhanced by hydrogen bonding of the chains by chemically bonded water molecules. After removal of excess water, the resulting dried mould retains the polyphosphate matrix which firmly binds together the water-insoluble particulate material. If excess water were not removed, the resulting wet mixture could be structurally weakened by the presence of water and would generally not be usable as a mould or core. In addition, the excess water would generate steam during the casting process which, as is well known in the art, would degrade the quality of the resultant casting.

Generally the principal component in a mould is a water insoluble particulate material which may be a refractory such as foundry sand e.g. silica, olivine, chromite or zircon sand or another water insoluble particulate refractory material such as alumina, an aluminosilicate or fused silica. The silica sands used for foundry work usually contain 98% by weight SiO_2 . The mould may also contain minor amounts of other additives designed to improve the performance of the mould.

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Preferably the binder comprises at least 0.25% by weight, and the particulate material comprises up to 99.75% by weight, of the total weight of the mixture of particulate material and the binder. More preferably the binder comprises from 0.5 to 50% by weight and the particulate material comprises from 99.5 to 50% by weight, of the total weight of the particulate material and the binder.

Preferably, the water soluble phosphate glass comprises from 30 to 80 mol% P_2O_5 , from 20 to 70 mol% R_2O , from 0 to 30 mol% MO and from 0 to 15 mol% L_2O_3 , where R is Na, K or Li, M is Ca, Mg or Zn and L is Al, Fe or B. More preferably, the water soluble phosphate glass comprises from 58 to 72 wt% P_2O_5 , from 42 to 28 wt% Na_2O and from 0 to 16 wt% CaO .

Such glasses include glasses of the following compositions in weight %:

	1	2	3	4	5	6
P_2O_5	70.2	67.4	64.6	61.8	59.0	60.5
Na_2O	29.8	28.6	27.4	26.2	25.0	39.5
CaO	-	4	8	12	16	0

As soluble glass, it is preferred to use a glass which has a solution or solubility rate of 0.1-1000 mg/cm²/hr at 25°C. The glass preferably has a saturation solubility at 25°C of at least 200 g/l, more preferably 800 g/l or greater, for phosphate glasses, and of at least 50 g/l for borate glasses.

The commonly available phosphate glasses are those from the binary system $Na_2O.P_2O_5$. The selection of glasses containing K_2O or mixed alkali metal oxides can be made on the same basis

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but glasses containing K_2O and/or mixtures of alkali metal oxides are less likely to be satisfactory as they are more prone to devitrification, and are also likely to be more costly.

A preferred glass is a phosphate glass from the binary system $Na_2O:P_2O_5$, with a molar ratio in the vicinity of $5Na_2O$ to $3P_2O_5$. Although such glasses can vary slightly in composition, we have satisfactorily used a glass containing P_2O_5 60.5 weight %, Na_2O 39.5 weight %. Such a glass has phosphate chains with an average value of $N = 4.11$, n being the number of phosphate groups in the chain. Glasses with longer chain lengths such as $n = 30$ when used as a binder give moulds with a satisfactory strength to withstand the conditions encountered in both handling the mould and using it for casting but can produce a mould which after use in certain casting processes such as die casting of aluminium requires relatively longer treatment with water to achieve disintegration and removal. Typically a mould made with a glass with a chain length of about 30 requires about 10 minutes soaking in water and 30 seconds flushing with water for removal, compared to less than 1 minutes soaking in water and 30 seconds flushing for a glass with a chain length of about 4. Thus where quick removal is required the shorter chain length glass is preferred.

We have carried out a variety of studies in order to assess the suitability of various water-soluble sodium polyphosphate glasses for use as binders. The following table shows compositions of some of the glasses tested:

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Glass Sample Number	Wt % P_2O_5	Wt % Na_2O	Water
1	69.0	30.5	Balance
2	67.0	32.5	Balance
3	65.0	34.5	Balance
4	63.0	36.5	Balance
5	60.5	39.0	Balance
6	58.0	41.5	Balance

We have noted that as the Na_2O content of the sodium polyphosphate glasses increases, the phosphate chain length generally becomes shorter and this in turn tends to increase the tensile strength of the core formed with the phosphate binder. We believe, without being bound by theory, that shorter phosphate chains may be better able to utilise hydrogen bonding and that the more chain end phosphate groups present may give stronger hydrogen bonding. We have also found with sodium polyphosphate glasses that as Na_2O content increases the dispersibility of a core employing such glasses as a binder tends to increase. We believe that this may indicate that the ability of partially hydrated glass to fully rehydrate and dissolve into solution is affected by small changes in composition.

In addition, we have found that as the Na_2O content increases, the viscosity of the solution of the sodium polyphosphate glass in water also tends to increase. We believe that this tendency for an increase of viscosity may possibly

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indicate the tendency to have hydrogen bonding in aqueous solution. This in turn may possibly indicate that viscosity may indicate the suitability of a given sodium polyphosphate glass to be effective as a binder to give good solubility and tensile strength. As specified hereinbefore, the glass must have a sufficiently high saturation solubility and solubility rate to enable it quickly and sufficiently to go into aqueous solution. We have found that all the glasses specified in the above Table have sufficient solubility rates and saturation solubility values. We have also found that an important practical aspect of the choice of polyphosphate glasses for forming cores is related to the shelf life which the core will be required to be subjected to in use. We have found that as the Na_2O content of the sodium polyphosphate glass increases, the tendency for the resultant core to be at least partially rehydrated by atmospheric moisture can increase, this leading to a consequential reduction in the tensile strength of the core thereby reducing the effective shelf life of the core. If the tensile strength is reduced in this manner the core may break prior to the casting process or may degrade during casting. Furthermore, we have found that the suitability of the various sodium polyphosphate glasses in any given casting process can depend on the temperature to which the resultant core is subjected during the casting process. We believe that this is because the temperature of the casting process can affect the binder in the core having consequential implications for the dispersibility of the core. For

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the use of a sand core during aluminium gravity die casting, the centre of a core may be subjected to temperatures of around 400°C but the skin of the core may reach temperatures as high as 500°C. The dispersibility of cores generally decreases with increasing temperature to which the cores have been subjected. In addition, the variation of dispersibility with composition may vary at different temperatures. We believe that indispersibility of the core after the casting process may be related to the removal of all combined water in the core which was previously bound with the sodium polyphosphate binder. In order to assess water loss of various sodium polyphosphate binders we carried out a thermogravimetric analysis on hydrated glasses. A thermogravimetric analysis provides a relationship between weight loss and temperature. Thermogravimetric analyses were carried out on a number of sodium polyphosphate glasses and it was found that in some cases after a particular temperature had been reached there was substantially no further weight loss which appeared to suggest that at that temperature all combined water had been lost from the glass. We have found that if this temperature is lower than the temperature to which the core is to be subjected to during a casting process, this indicates that the core may have poor post-casting dispersibility resulting from excessive water removal from the core during the casting process. A suitable core binder also required a number of other features in order to be able to produce a satisfactory core, such as dimensional stability, absence of distortion during the casting process, low gas evolution and low surface erosion in a molten metal flow.

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Overall, it will be seen that there are a variety of factors which affect the choice and suitability of a binder. For any given application, the choice of a binder can be empirically determined by a trial and error technique. However, the foregoing comments give a general indication as to the factors affecting the properties of the binder. What is surprising is that from the combination of these factors, an inorganic binding material, such as a polyphosphate, can be subjected to the temperatures involved in a casting process and still remain readily soluble so as to enable a sand core which is held together by a binder of the polyphosphate material rapidly to be dispersed in water after the high temperature casting process.

According to the method of the invention the mixture of particulate material and binder are heated to a temperature in excess of 100°C prior to being formed into the desired shape. Preferably, the particulate material, e.g., foundry sand, is heated prior to being mixed with the binder. This enables a supply of hot sand to be maintained in reserve so that the period for which the mixture of sand, binder and water needs to be heated together may be reduced. If the sand is prior heated to a temperature of 100°C or greater then when this is mixed with the binder the resultant mixture will have a temperature close to or even greater than 100°C. The binder may also be heated prior to mixing although care should be exercised to ensure that water is not excessively volatilised off from the binder composition.

Following the heating step, the mixture is formed into the desired shape. This may be achieved by blowing the heated mixture into a suitable core box using a core blower. Preferably, the temperature of the mixture is maintained during transfer to the core box.

After the mixture has been formed water is then

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removed from the formed mixture with air at a temperature in excess of 100°C. Typically, the core mould is provided with heating means, such as an electrical heater, so that the temperature of the formed mixture can be controlled. Air is passed into the core box to effect removal of water from the mixture. The air may be heated up to a temperature of about 250°C. Typically, however, the air temperature will be maintained at about 150°C.

When the particle size of the particulate material is relatively small, a relatively large amount of binder will be required in order to ensure that the binder matrix binds together the larger number of particles which provide a correspondingly large surface area.

It has been found where the amount of binder is relatively small as compared to the quantity of sand or other particulate material, it is preferable to introduce the water and glass in the form of a solution of the glass in water. Typically, for a coarse foundry sand (i.e., AFS 50) we have found that the preferred weight ratio of glass:water is 1:0.75-1 when producing a glass solution,

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and the equivalent glass:water ratio for a fine foundry sand (i.e., AFS 100) is 1:1-1.5. The glass in a powdered form is simply added to water and mixed with a high shear mixer to achieve full solution. A portion of the solution is then added to the refractory particulate material and mixed thoroughly before e.g., blowing the mixture into a core box preheated to 80°C with compressed air at a pressure of about 80 pounds per square inch, and then purging with compressed air at ambient temperature for about 50 seconds. Cores with good handling strengths are obtained in this manner. Moulds can also be formed.

An embodiment of the invention will now be described with reference to the following drawing in which Figure 1 is a schematic layout for apparatus arranged to carry out the method of the present invention.

Referring to Figure 1 a hopper 1 receives binder and feeds the binder to a heated continuous mixer 5. During transferal from the hopper 1 to the mixer 5, the binder may be heated, for instance by a ribbon heater 4. Sand is fed from a hopper 2 to a heater 3. The heated sand is then fed to the continuous mixer 5 where it is mixed with the binder. The mixer 5 is heated and insulated to maintain the temperature of the binder/sand mix above 100°C.

The sand binder mix is fed through a buffer hopper 7 to a heated screw feeder 8. From the screw feeder discrete amounts of mix are fed via a slide valve 9 to a shooter head 10. From the shooter head the mix is blown into a core box 11 to form a core. It should

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be noted that in addition to the continuous mixer, hopper 7, screw feeder 8 and the shooter head 10 are all heated and insulated to ensure that the binder sand mix is maintained at a temperature in excess of 100°C.

It is essential that the water content of the binder/sand mix remains above a particulate level prior to being blown into the core box to prevent the mix from hardening as it passes through the machinery. This is achieved by keeping the mix in a saturated atmosphere of steam from the mixer 5 through to the shooter head. A vent 6 in the mixer prevents the atmosphere being pressurized and each individual apparatus from the mixer 5 to the shooter head 10 is sealed to prevent water losses.

The core box 11 is heated and purged with hot air typically at a temperature of 150°C to remove the water held within the mix. After a relatively short time period substantially all the water has been removed from the core, and the core is now suitable for use in making foundry castings.

To illustrate the advantages of the present invention the following shows the purge times for cores formed according to a conventional method and according to the present invention.

Core weight (g)	Conventional method (sec)	Present method (sec)
500	40	<5
1000	60	8
1500	90	10

Thus according to the present invention purge times are significantly reduced.

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EXPERIMENTAL

A series of experiments were performed to determine the effect of sand/binder mixture temperature upon hardening of 75mm diameter cylinder cores of length 12.5cm.

Binder Preparation

The polyphosphate glass was dissolved in water to give a 50% solution (w/w). When cool, a hot strength additive comprising sodium aluminium silicate in an amount of 10% by weight based on the weight of the solid binder was mixed in to give a slurry.

Sand/Binder Preparation

The binder slurry was added to Chelford AFS 60 (4.4% w/w) and intimately blended using a Ridsdale mixer.

Core Preparation

Portions of the sand/binder mixture (1.0kg) were heated to temperatures in the range 50°C to 110°C in a microwave oven. A sealed container was used to prevent evaporative losses.

The heated mixture was hand rammed into the preheated cylinder mould and final compression achieved using a pneumatic piston. A purge head was clamped onto the core mould and heated air passed through the mixture for predetermined periods of time.

Upon removal from the mould, cylinders were assessed for degree of hardness by determining the weight of unhardened material present.

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Observations

A plot of percentage hardened profile vs purge time, in seconds, for different mixture temperatures (Figure 2) clearly indicates little difference in the effect of increasing the mixture temperature through 50°C (x-x), 60°C (o-o), 70°C (□-□), 80°C (▽-▽) and 90°C (△-△). Hardening times were in the range 60 sec to 100 sec.

With the mixture temperature elevated to 100°C, hardening time was reduced to 30 sec (+++). A further reduction in hardening time to 20 sec (◇-◇) was achieved by heating the sand/binder mixture to 110°C. A plot of purge time (seconds) to 100% hardness vs mix temperature is shown in Figure 3.

Operating Conditions

Mould temperature	107°C
Purge Air temperature	105°C
Purge Air flow	18dm s ⁻¹
Purge Air pressure	100 p.s.i.

Conclusions

Rapid hardening was achieved when a significant proportion of the energy to meet latent heat of evaporation requirements has been supplied to the mixture prior to its addition to the mould.

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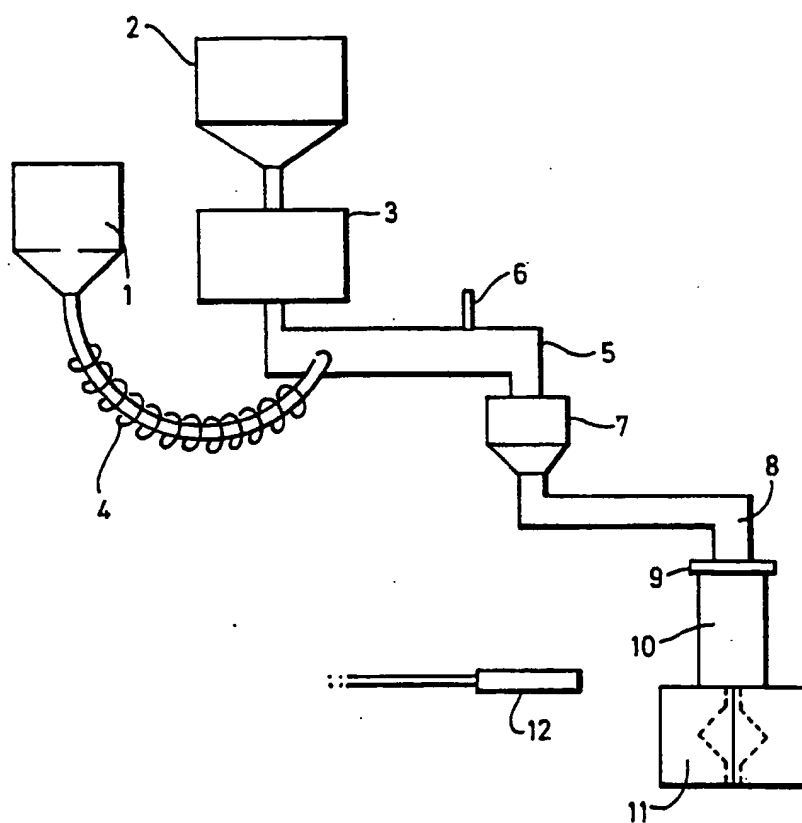
CLAIMS

1. A method for making a mould used in the manufacture of foundry castings, the method comprising the steps of:
 - (a) providing a water insoluble particulate material;
 - (b) combining the particulate material with a binder;
 - (c) heating the mixture of particulate material and binder to a temperature in excess of 100°C;
 - (d) forming the particulate material and binder mixture into a desired shape;
 - (e) removing water from the mixture with air at a temperature in excess of 100°C.
2. A method as claimed in claim 1, wherein the water insoluble particulate material is heated prior to being mixed.
3. A method as claimed in claim 1 or claim 2, wherein the steps (b) to (d) are carried out in a saturated atmosphere of steam.
4. A method as claimed in any preceding claim wherein the water insoluble particulate material is foundry sand.
5. A method as claimed in any preceding claim wherein the binder includes polyphosphate chains and/or borate ions.
6. A method as claimed in claim 5, wherein the polyphosphate chains and/or borate ions have been respectively derived from at least one water soluble phosphate and/or borate glass.
7. A method as claimed in claim 6 wherein in step (b) the binder which is mixed with the particulate material is in the form of an aqueous solution of the at least one water soluble glass.

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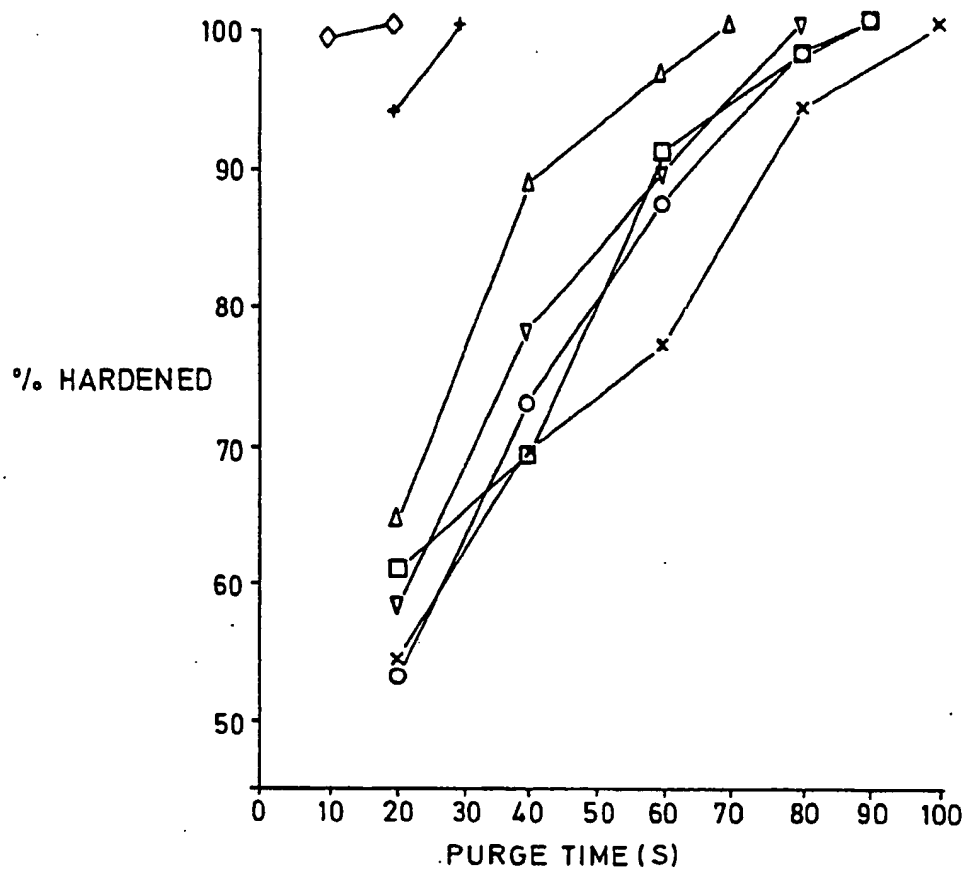
8. A method as claimed in claim 6 wherein in step (b) the binder which is mixed with the particulate material is in the form of particles of the at least one water soluble glass and the polyphosphate chains and/or borate ions are formed by mixing water with the mixture of particulate material and glass particles.
9. A method as claimed in any preceding claim wherein in step (b) the binder comprises at least 0.25% by weight, and the particulate material comprises up to 99.75% by weight of the total weight of the mixture particulate material and the binder.
10. A method for making a mould used in the manufacture of foundry castings substantially as hereinbefore described with reference to, and as illustrated in Figure 1.

FIG. 1



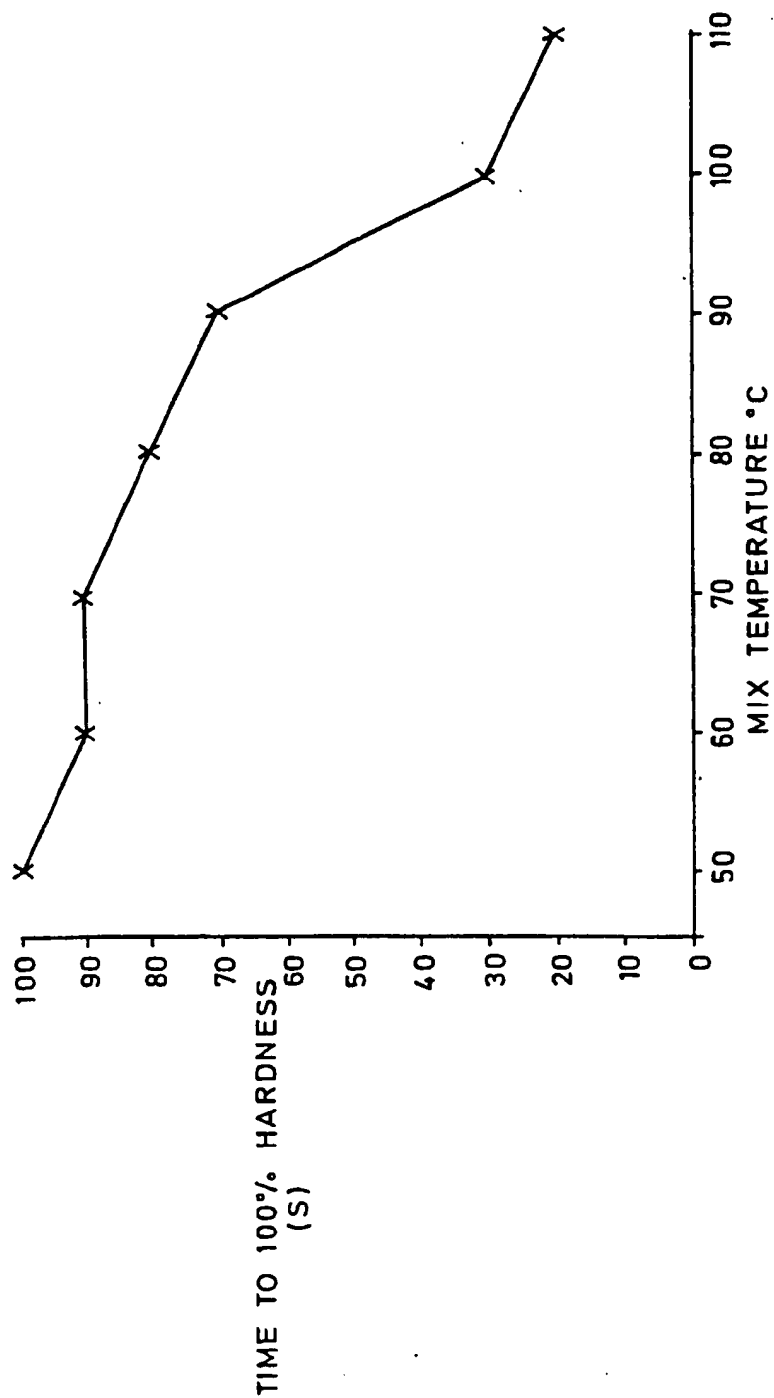
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FIG. 2



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FIG. 3



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/00636

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B22C5/08; B22C5/04; B22C9/12		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B22C	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,P	WO,A,9 206 808 (PILKINGTON CONTROLLED RELEASE SYSTEMS LIMITED) 30 April 1992 see example 4 see claims	1-10
Y	GB,A,2 045 132 (VEB KOMBINAT GIESSEREIANLAGENBAU UND GUSSEZEUGNISSE GISAG) 29 October 1980 * whole document *	1-4
Y	US,A,3 537 186 (RENNERFELT) 3 November 1970 see column 1, line 58 - line 67	1-4
	-/--	
<p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
01 JULY 1993	20.07.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	RIBA VILANOVA M.	

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claims No.
A	GB,A,1 213 232 (NAUCHO-ISSLEDOVATELSKY PROEKTNO-KONSTRUKTORSKY INSTITUT TEKHNOLOGII) 25 November 1970 see page 1, line 17 - line 45 see claim 1 -----	1

Form PCT/ISA/210 (extra sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9300636
SA 71931

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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GB-A-2045132	29-10-80	DE-A- 3007964	11-12-80
US-A-3537186	03-11-70	GB-A- 1238229	07-07-71
GB-A-1213232	25-11-70	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82